



Clean Energy Research at the University of South Carolina

Dr. Ralph E. White, PI

James A. Ritter, co-PI and Presenter
University of South Carolina

May 24, 2005

Project ID #ST9 White

This presentation does not contain any proprietary or confidential information.



Overview

Projects

- Project I. Low Temperature Electrolytic Hydrogen Production (Dr. John Weidner)
- Project II. Development of Complex Metal Hydride Hydrogen Storage Materials (Dr. James Ritter)
- Project III. Hydrogen Storage Using Chemical Hydrides (Dr. Michael Matthews)
- Project IV. Diagnostic Tools for Understanding Chemical Stresses and MEA Durability Resulting from Hydrogen Impurities (Dr. John Van Zee)
- Project V. Durability Study of the Cathode of a Polymer Electrolyte Membrane Fuel Cell (Dr. Ralph White)

Timeline

- Project start date June 1, 2004 (1st year project)
- Project end date November 30, 2005
- Five co-projects initiated
- 30 Percent complete

Budget

- Total project funding
 - DOE share \$2,158,370
 - contractor share \$539,593
 - \$ split nearly equally among the five projects

Safety

- The most significant hydrogen hazards associated with this project are:
 - High reactivity of solid chemical hydrides when exposed to humidified air
 - Toxicity: Avoid ingestion or contact with eyes and mucous membranes
- The approach to deal with this hazard is:
 - Handle hydrides in an inert atmosphere within a glove box
 - Use small quantities for laboratory experiments
 - Blanket reactor with inert gas



Technical Barriers and Targets

Hydrogen Storage

DOE Targets:

- 2005 – 1.5 kWh/kg (4.5 wt %), 1.2 kWh/L, \$6/kWh
- 2010 – 2 kWh/kg (6 wt %), 1.5 kWh/L, \$4/kWh
- 2015 – 3 kWh/kg (9 wt %), 2.7 kWh/L, \$2/kWh

Technical Barriers:

- higher system weight, high volume
- high cost of storage
- durability of at least 1500 cycles
- lower than expected energy efficiency
- long refueling time

Fuel Cell

DOE Targets:

- \$30/kW for transportation
- 5,000 hr lifespan
- 40 to 80 °C operating range
- electrode performance

Technical Barriers:

- high system weight and volume
- high cost
- unproven durability
- air, thermal and water management

Nuclear H₂ Production

DOE Targets:

- improved materials
- create reaction database
- more efficient system designs

DOE Barriers:

- high-temperature, corrosion resistant materials
- chemical reaction data
- system design



Project II: Development of Complex Metal Hydride Hydrogen Storage Materials (Dr. James Ritter)

Objectives

- Study the effect of different metal dopants and co-dopants on dehydrogenation (discharge or desorption) of NaAlH_4
- Study the effect of different carbon materials as a co-dopant with Ti and Al powder on dehydrogenation (discharge or desorption) and hydrogenation (charge or adsorption) of NaAlH_4
- Study the effectiveness of a new sonochemical pretreatment method for improving the dehydrogenation and hydrogenation kinetics of NaAlH_4
- Study the reversibility of LiAlH_4 and $\text{Mg}(\text{AlH}_4)_2$ when doped with Ti under conditions similar to those that are effective with Ti-doped NaAlH_4

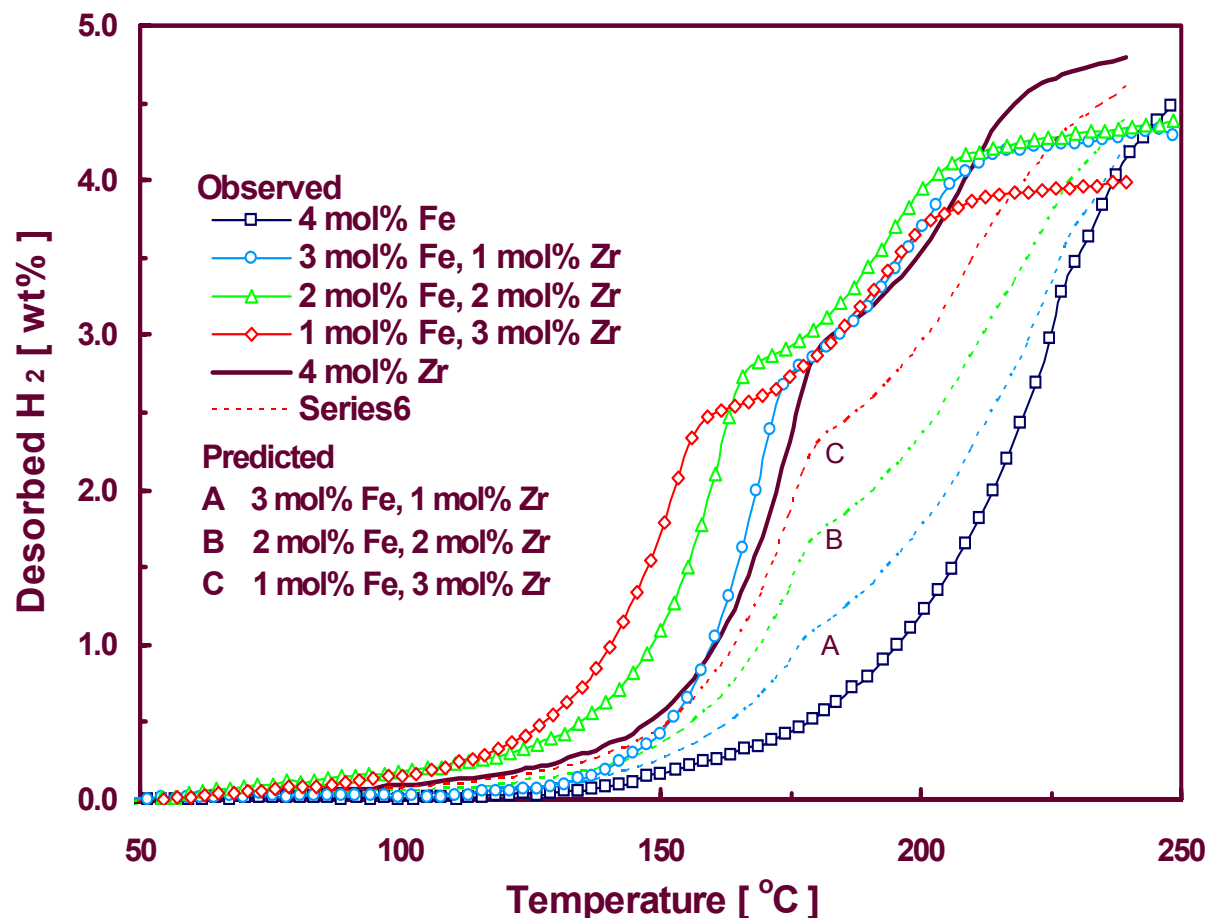


Approach

- prepare samples of NaAlH_4 , LiAlH_4 and $\text{Mg}(\text{AlH}_4)_2$ using a conventional wet or new sonochemical doping procedure prior to high energy ball milling
 - ❖ samples possibly doped with Ti, Zr, Fe, Al powder and or various forms of carbon
- cycle the prepared samples in a unique high pressure cycling facility to obtain qualitative discharge and charge kinetics
- discharge the prepared samples in a TGA to obtain quantitative kinetics and capacities under temperature programmed and constant temperature desorption modes
- characterize the prepared samples in terms of their dehydrogenation and hydrogenation kinetics, capacity and reversibility



TPD: Synergistic Effects of Co-Dopants, Zr and Fe, on the Dehydrogenation of NaAlH_4



Is there a combination of early and late transition metals that could instill superior performance compared to a single metal dopant like Ti? This supposition is being explored.

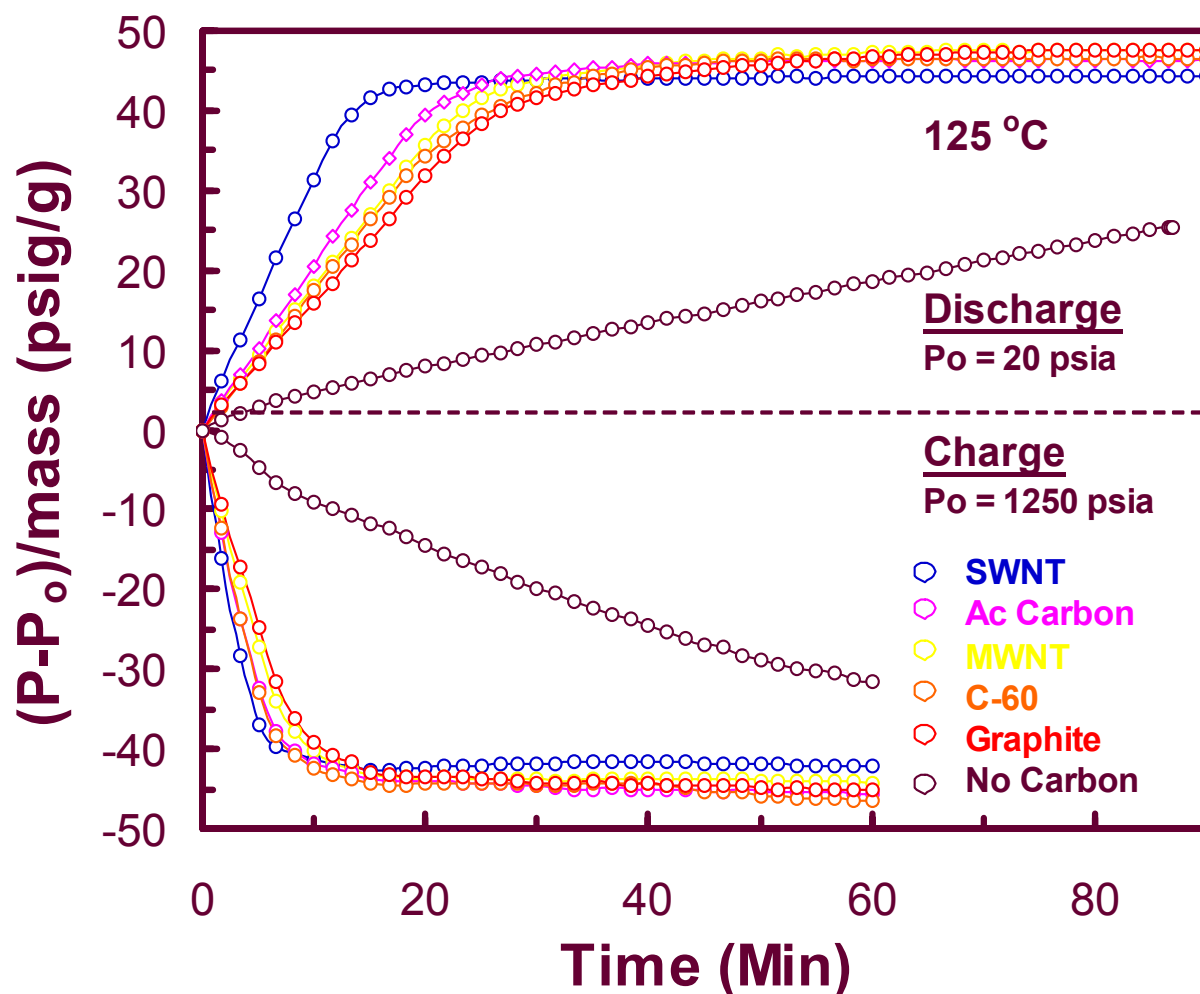
- Predicted TPD is expected behavior of a simple physical mixture, i.e., linear combination, of the two metal dopants.
- Observed TPD is the actual synergistic behavior of the two metal dopants.
- Observed synergism, in most cases, is **much better** than 4 mol% Zr alone!
- Consistent with the “metal-metal bond polarity” concept, in that **Zr and Fe** are from **opposite sides** of the periodic table.
- Ti and Fe exhibit similar behavior; but not Ti and Zr.



Influence of Different Carbon Materials on Dehydrogenation and Hydrogenation Rates of Carbon-Doped and Cycled NaAlH_4

All samples doped with 2 mol% Ti and 5 wt% Al and cycled 5 times

All samples containing carbon doped with 10 wt%



Samples doped with Ti and carbon consistently showed faster dehydrogenation and rehydrogenation rates over just Ti-doped samples.

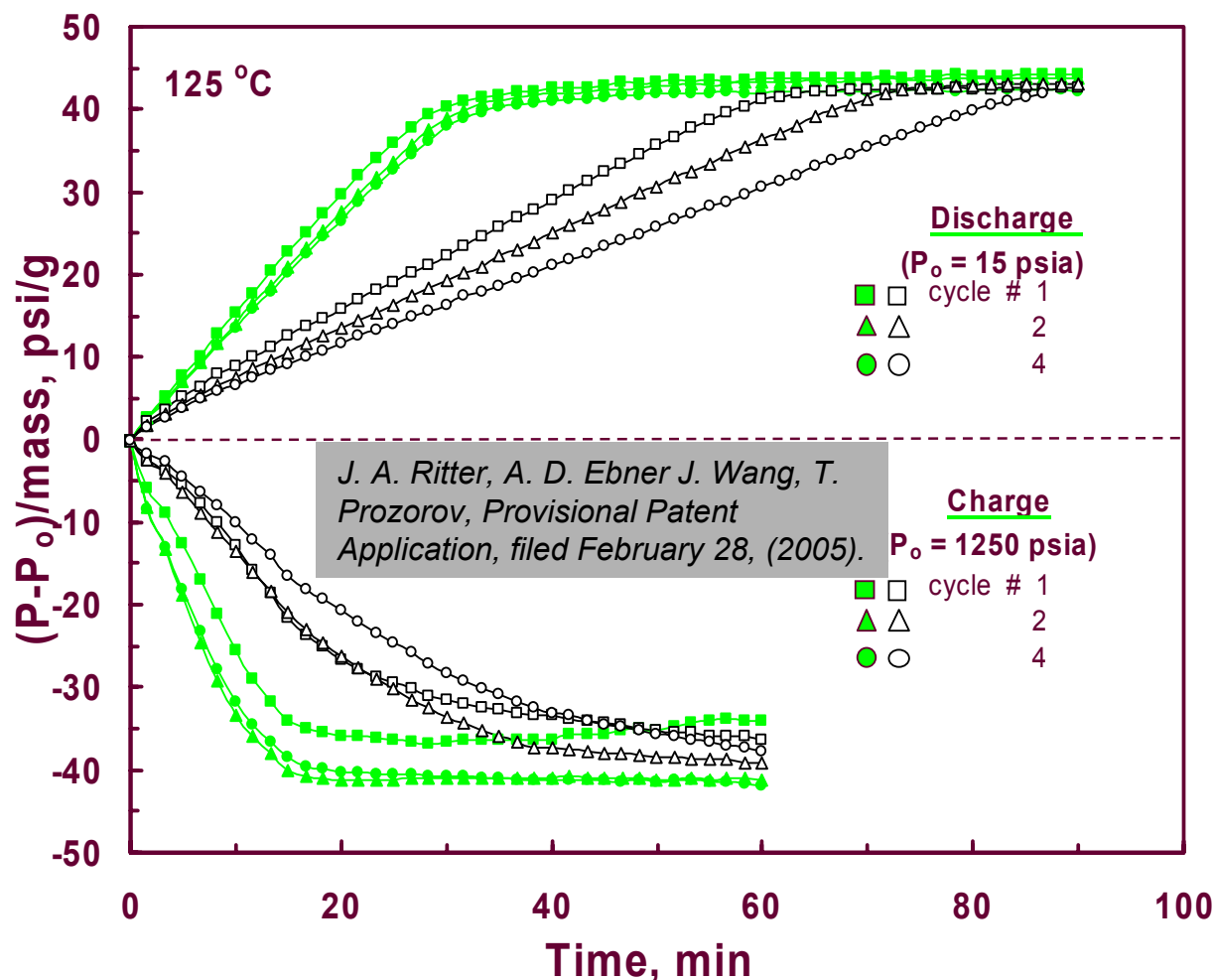
Samples doped with SWNTs and graphite showed the strongest and weakest effects, respectively.

At $T = 125$ °C and $P = 1,250$ psia charging of Ti and carbon doped materials occurs within 10 min!



Influence of Sonochemical PreTreatment on Hydrogenation and Dehydrogenation Rates During Cycling

Ball milled samples of NaAlH_4 wet doped and sonochemically doped in decalin with THF, all doped with 2 mol% Ti. Filled symbols correspond to the sonochemically doped sample; empty symbols correspond to the wet doped sample.



Influence of sonochemical PT on both dehydrogenation and hydrogenation kinetics, is clearly observed. The time for charging is markedly decreased again by a factor of four, from about 60 to 15 min.

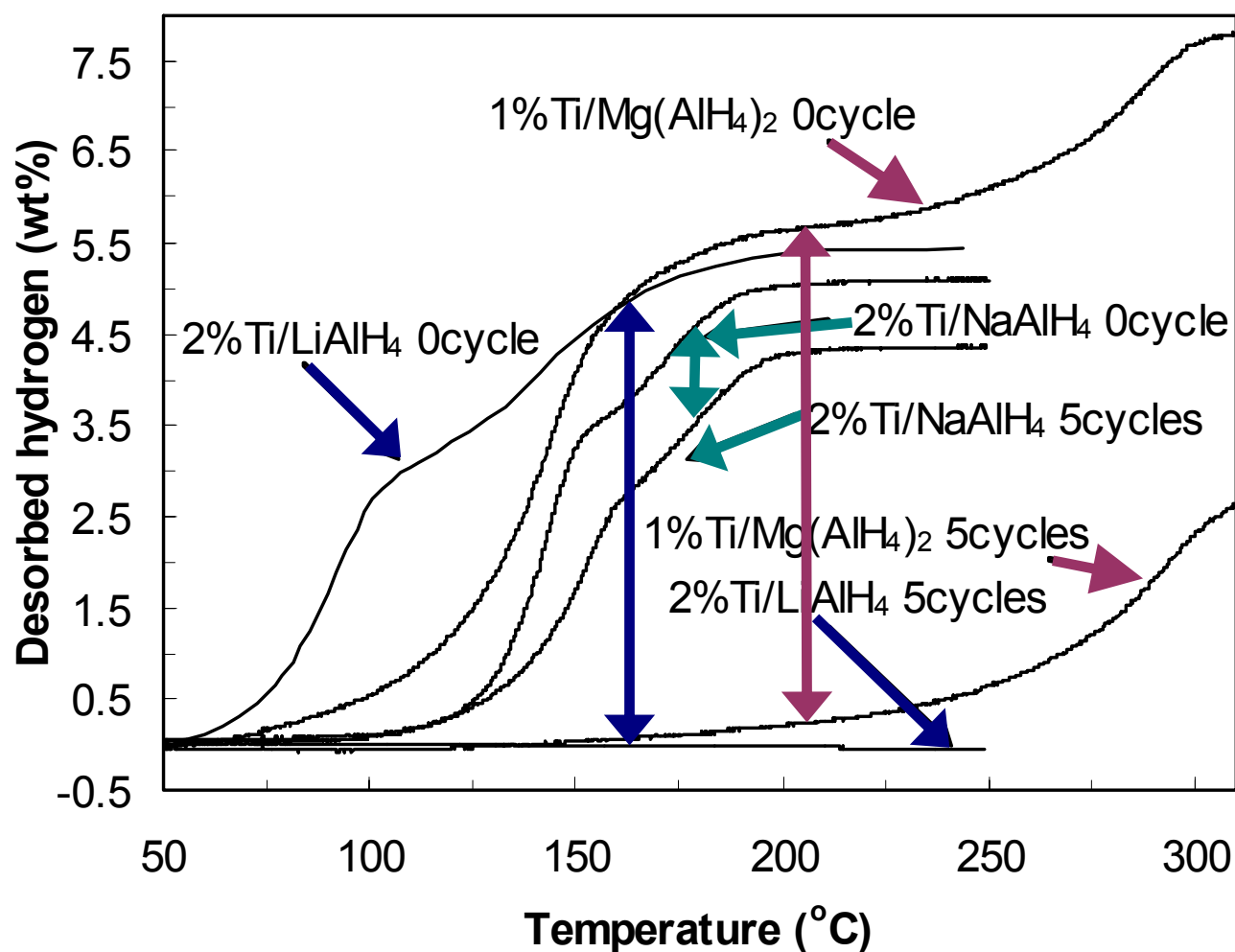
Again, these results may represent the best charge kinetics to date for a sample of NaAlH_4 doped with as little as 2 mol% Ti.



Comparison of 0th with 5th Discharge Cycle of Ti-Doped NaAlH₄, LiAlH₄ and Mg(AlH₄)₂

Rate = 5 °C/min

J. Wang, A. D. Ebner and J. A. Ritter,
Adsorption, 11, 811-816 (2005).



Five discharge (4 hrs) and charge (8 hrs) cycles carried out **between 50 and 1,200 psig at 125 °C for Na alanate BM 120 min**, **between 50 and 2,100 psig at 140 °C for Li alanate BM for 20 min**, and **between 50 and 1,500 psig at 150 °C for Mg alanate BM 15 min**.

Under these conditions, only the Na alanate system is observed to be reversible! The Li and Mg alanates systems do not exhibit any reversibility.



Future Research Directions

FY05 – FY06

- complete Raman study of Ti-doped NaAlH_4 with Dr. Williams
- continue to explore bimetallic and metal-carbon catalyzed alanates
- continue to explore new sonochemical pretreatment method possibly as an alternative to ball milling metal-doped alanates
- continue to work with Dr. Angerhofer at UF on carrying out high field EPR studies with doped alanates
- continue to work with Dr. Rasolov at USC on *ab initio* studies of TiCl_3 - NaAlH_4 clusters
- continue to synthesize and study the reversibility of other metal doped alanates and boronates, and to carry out a thermodynamic analysis to explain their inherent stability



Project III: Hydrogen Storage Using Chemical Hydrides (Dr. Michael Mathews)

Objectives

- Develop hydrogen storage and delivery technology based on steam + chemical hydrides for automotive fuel cell applications
 - Evaluate novel steam + solid chemical hydride reaction as basis for on-demand production of hydrogen
 - Compare experimental data to FreedomCAR targets
 - Mass efficiency of reaction (8MAA)
 - Hydrogen production rate / kinetic data (12MAA)
 - Analysis of water utilization of reactor and characterization of hydration characteristics of products (14MAA)
 - Prototype design development (16 MAA)



Approach

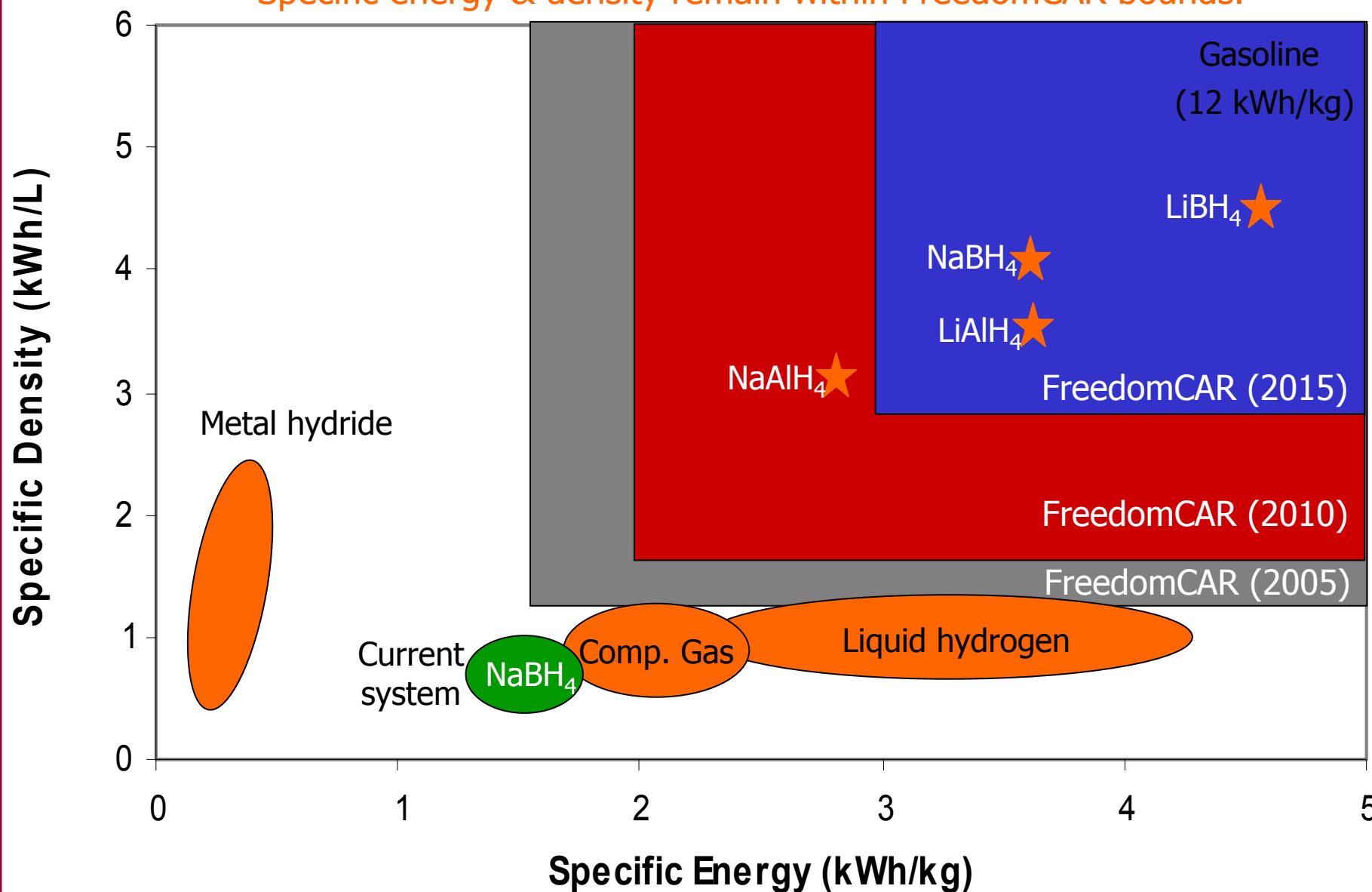
- Hydrolyze chemical hydrides with dry steam, rather than aqueous catalytic process
 - Chemically simple reaction
 - Humid H_2 gas product
 - Hydride reactants and products are dry
 - Minimal water inventory in the reactor
 - Autothermal integration: use heat of reaction to produce steam
- Operate reactor at low temperatures ($100\text{ }^{\circ}\text{C}$ – $150\text{ }^{\circ}\text{C}$) and pressures
- Conduct basic research on the reaction to utilize water efficiently and maximize H_2 delivery rate
 - Translate results to prototype design via mathematical model



Approach

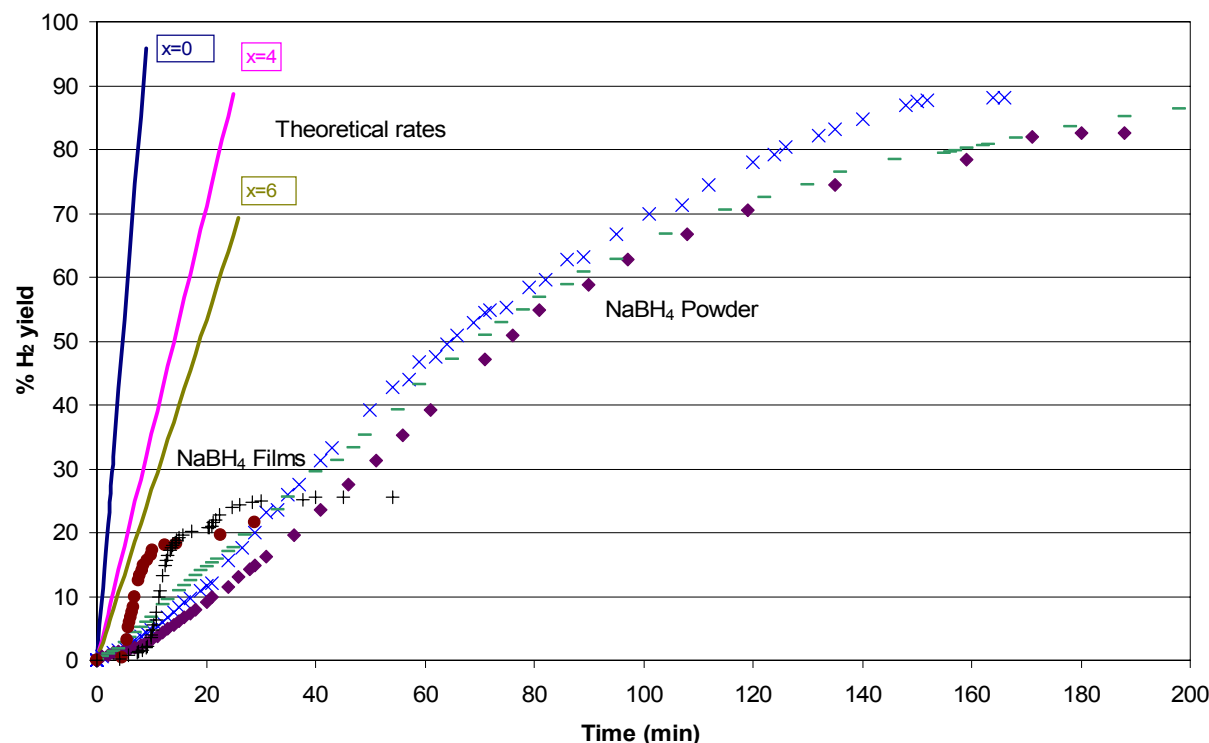
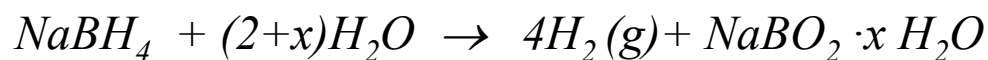


Design system using steam hydrolysis technology so that total system Specific energy & density remain within FreedomCAR bounds.





Films of Recrystallized NaBH_4 Give Improved Initial Rates



x is an indirect measurement of the efficiency of water utilization of the reaction

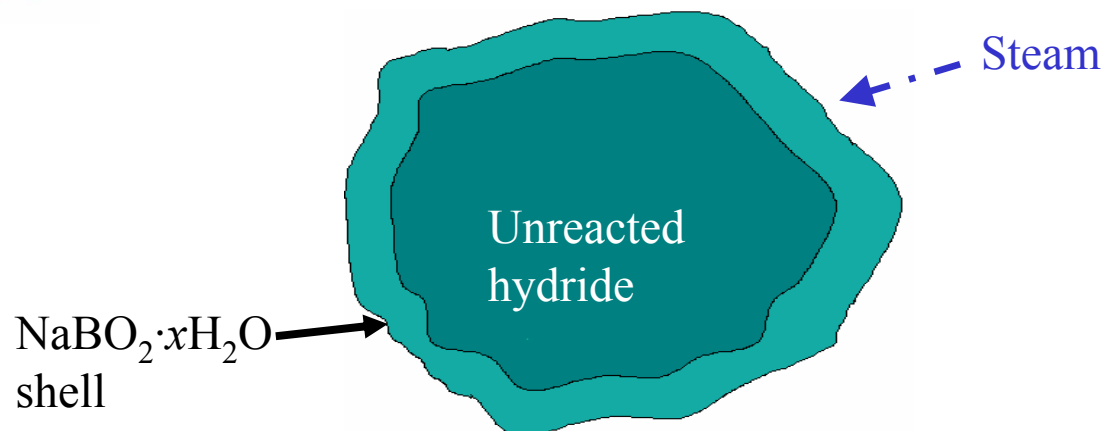
- Thin films give higher initial rates ($x = 2-3$)
- Yields $< 100\%$ are attributed to channeling within reactor and insufficient reactant contact at longer times.

FreedomCar Gravimetric Efficiency

	Target (wt%)	Equiv. x
2005	4.5	4
2010	6.0	3
2015	9.0	1

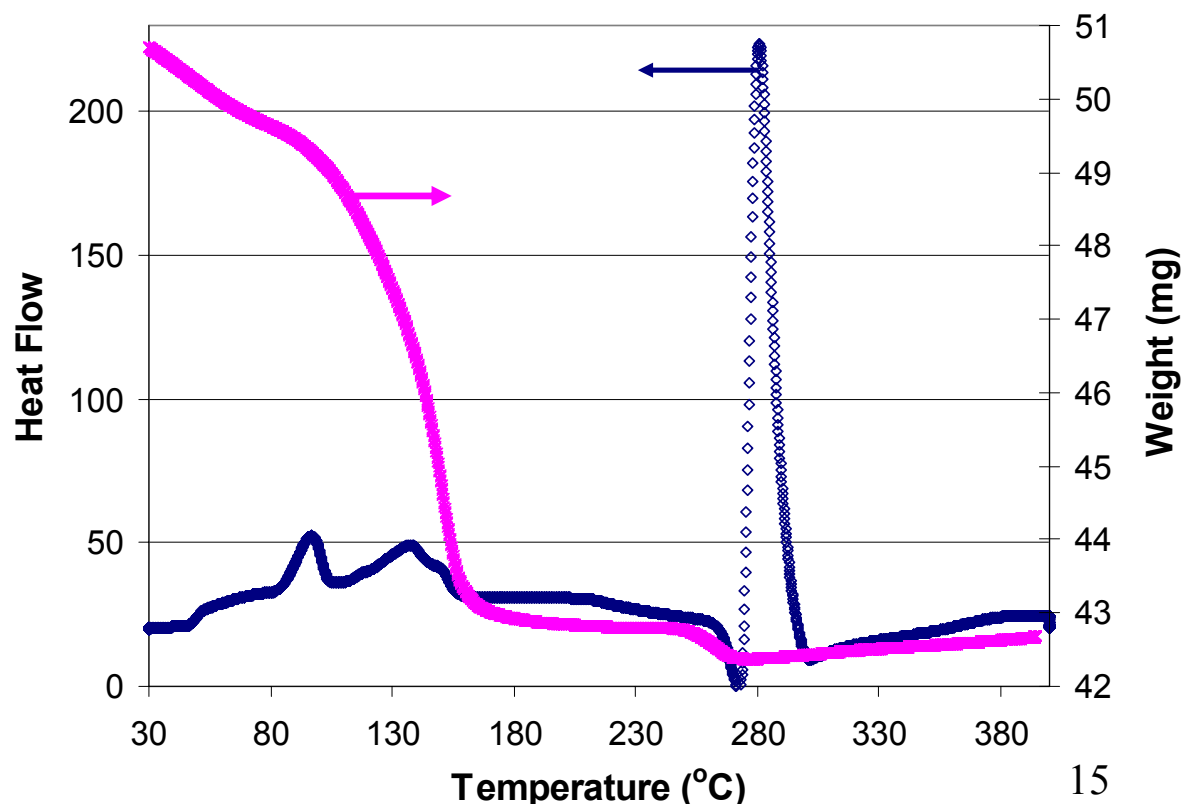


Water Utilization and Product Characterization



- NaBO₂·xH₂O product is a dense solid
 - Dense by-product causes mass transfer limitation
 - Highly hydrated byproducts
- Wastes water and decreases gravimetric efficiency

- Investigate hydration properties of products with Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)
 - TGA: 17 wt% loss associated with H₂O loss by borate product
 - DSC: peak indicates phase transition in products





Future Research Directions

FY05

- Steam/solid NaBH_4 system
 - Obtain improved gravimetric efficiency of reaction
 - Liberate H_2 wt% > 4.5 by 4/30/2005
 - Measure intrinsic kinetic rate of reaction under different operating temperatures, pressures and reactant preparations
 - Full flow of H_2 in < 10 sec by 10/30/2005
 - Clarify the effect of particle size on reactant contact and mass transfer
 - Determine hydration characteristics of products in order to improve gravimetric efficiency and understand shell formation
- Investigate additional solid hydride systems
 - Evaluate additional hydrides based on FreedomCAR requirements

FY06

- Submit description of prototype system design
 - Design will be based on laboratory-scale experiments
 - Design will be evaluated according to FreedomCar targets such as mass and volumetric efficiency and startup dynamics



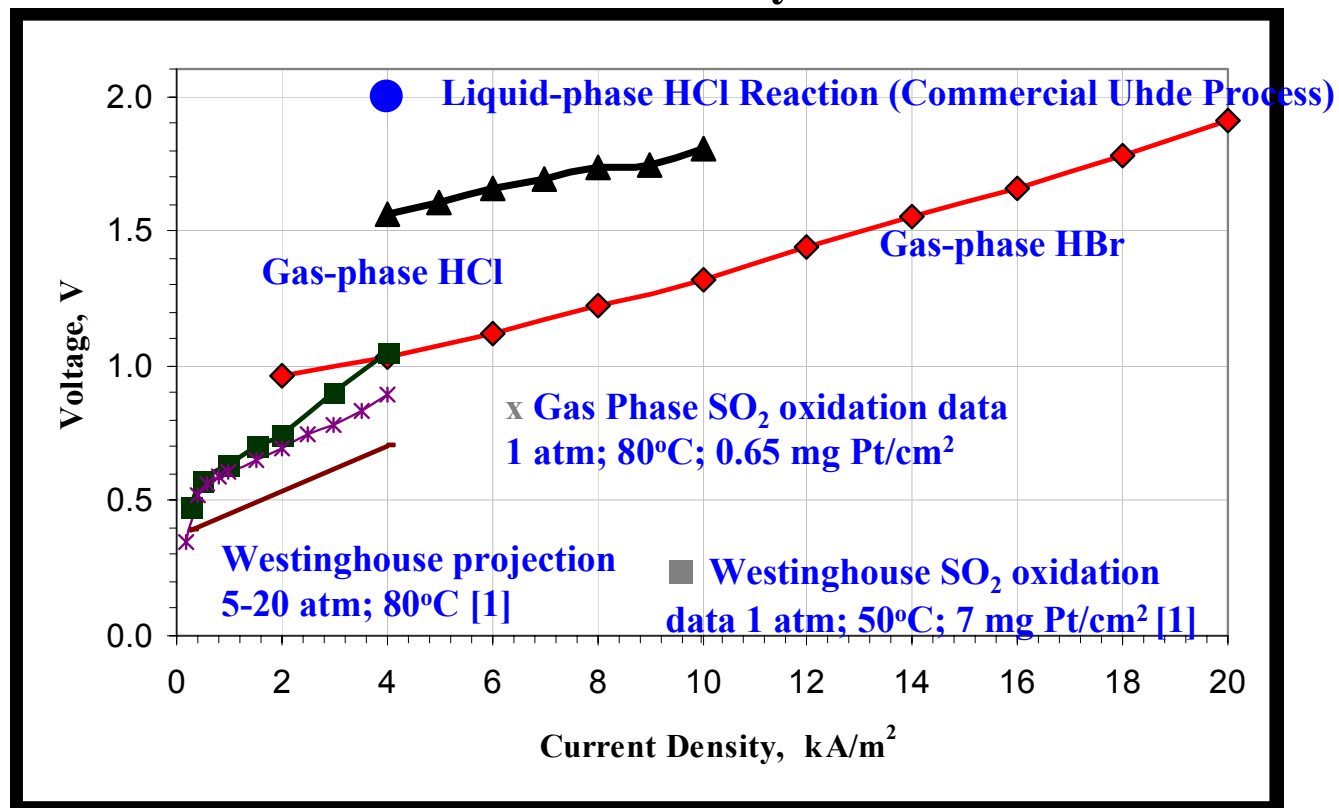
Project I: Low Temperature Electrolytic Hydrogen Production (Dr. John Weidner)

Objective

- Develop a *gas phase* proton exchange membrane (PEM) electrolyzer to convert
 - HBr to Br₂ and H₂
 - SO₂ to H₂SO₄ and H₂
- Provide
 - Higher current densities (i.e., small, low cost electrolyzer)
 - Better thermal management
 - Lower voltages (i.e., higher efficiencies)
 - Lower reactant crossover (i.e., reduced poisoning)
 - Better control of product purity
 - Lower catalyst loadings



Gas Phase Electrolysis Delivers



[1] P.W. Lu *et. al.*, *J. Appl. Electrochem.*, 347 (1981).

Future Work

FY05 – FY06

- quantify the relationships among design and operating parameters
- integrate electrolyzer information into the system-level Aspen model developed by SRNL
- quantify the extent of sulfur poisoning and attempt to minimize its affect
- decrease current and increase voltage for SO₂ oxidation. (Goal: 5 kA/m² @ 0.6V)
- improve water management



Project IV: Diagnostic Tools for Understanding Chemical Stresses and MEA Durability Resulting from Hydrogen Impurities (Dr. John Van Zee)

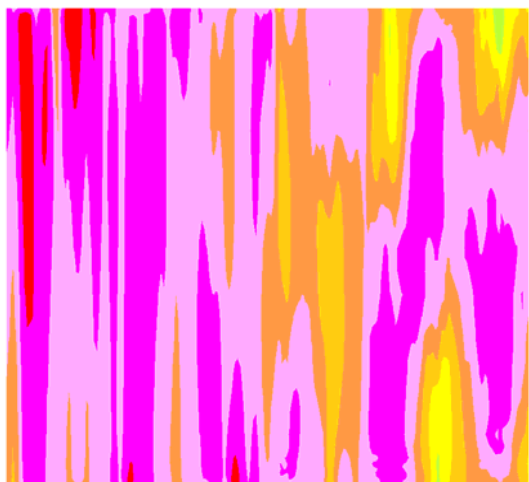
Objectives

- Develop Predictive Capabilities to Assess Durability and Failures Resulting From H₂ Impurities
 - H₂S, NH₃ as models for catalysts poisoning and ionomer attack
 - Compare with Computational Fluid Dynamic Models for CO Poisoning
- Provide
 - Methodology for 3-D predictions of poisons
 - Rate constants and mechanisms for poisoning
 - Predictions and verifications of local distribution of poisons
 - Improved tolerance by adjustment of operating conditions
 - Understanding of dosage, concentration, and interaction effects

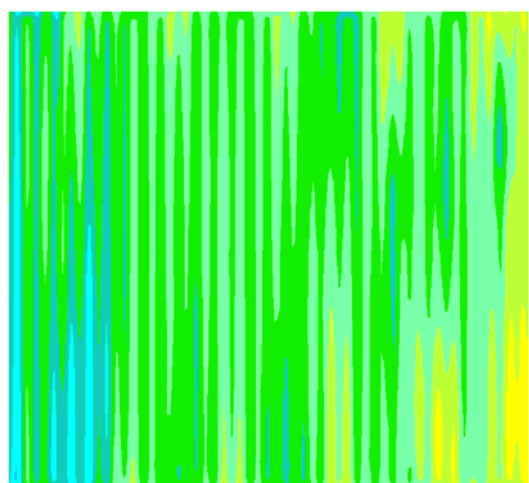


Significant Results/Approach

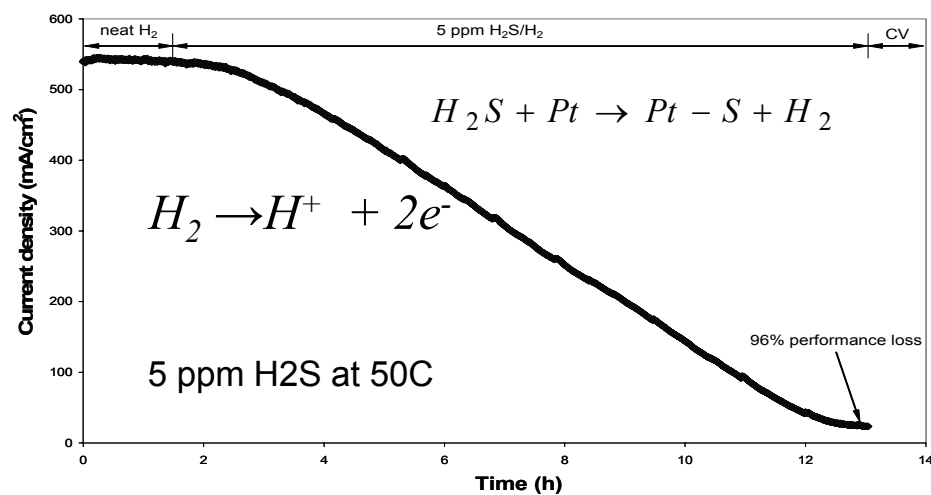
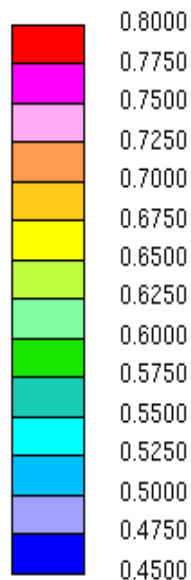
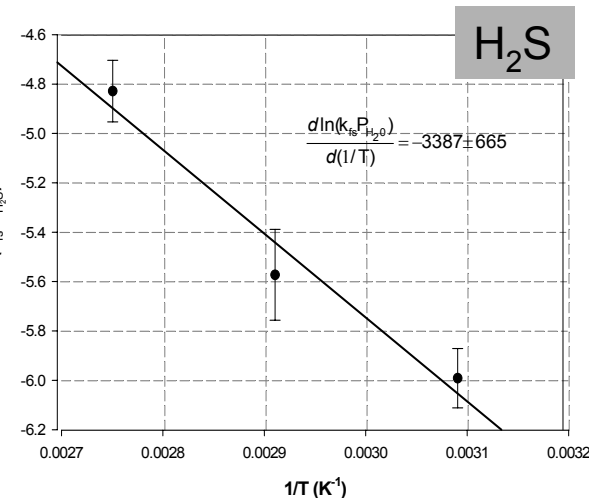
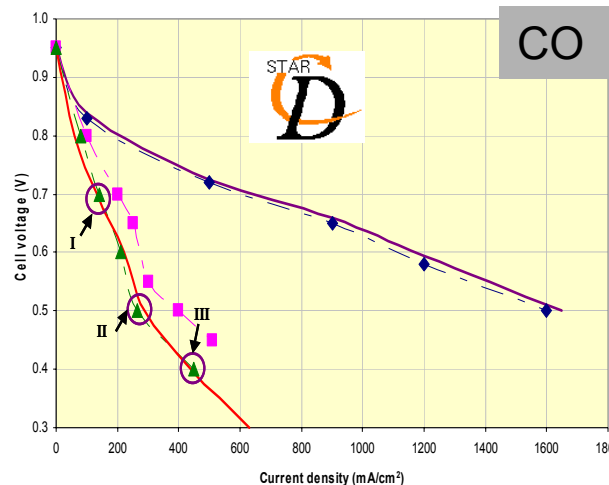
Local CO coverage distribution on anode catalyst surface at selected points for 1000 ppm CO; similar distributions are expected for H₂S data below.



Point # I: CO_{avg} = 0.75 at V_{cell} = 0.7 V



Point # II: CO_{avg} = 0.6 at V_{cell} = 0.5 V





Project V: Durability Study of the Cathode of a Polymer Electrolyte Membrane Fuel Cell (Dr. Ralph White)

Motivation

- kinetics of the O_2 reduction reaction (ORR) at the cathode of a PEM fuel cell is usually described by Tafel equation, which predicts a straight line on a plot of the electrode potential versus the logarithm of ORR kinetic current (e.g., E vs. $\ln I_k$).
- actual ORR kinetics do not follow the Tafel equation because a plot of E vs. $\ln I_k$ usually yields a curve, rather than a straight line, with two slopes
- this will inevitably lead to errors in the evaluation of the relative importance of other transport phenomena, e.g., O_2 diffusion

Objectives

- ❖ to develop a semi-empirical equation to account for the ORR kinetic current, I_k
- ❖ to evaluate the goodness of using this equation in fitting the Rotating Disk Electrode (RDE) data measured on a catalyst used widely to make a PEM fuel cell

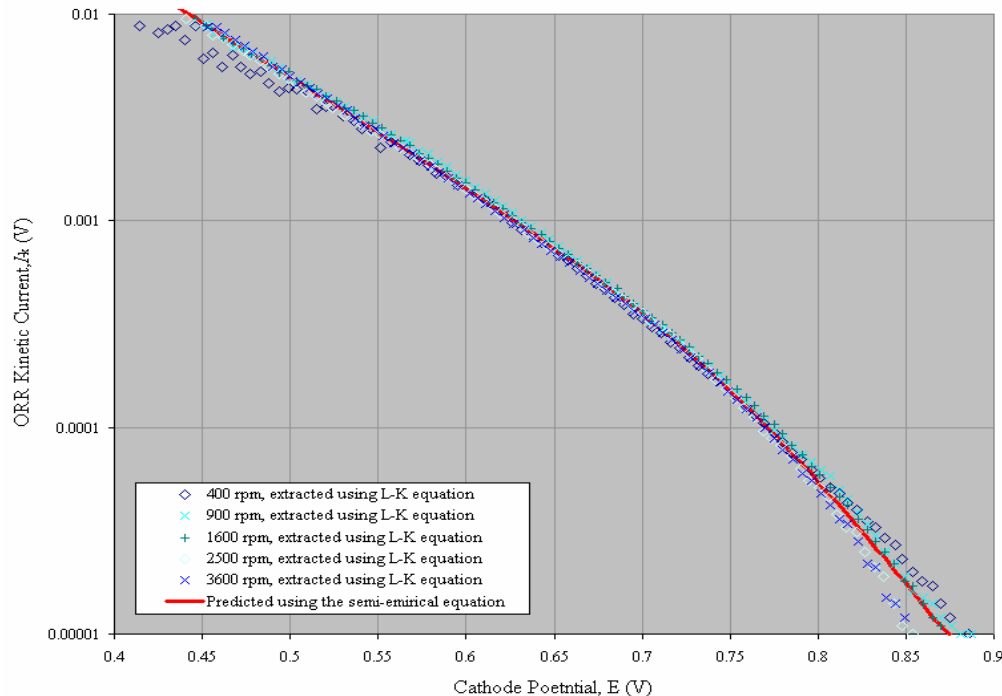


Significant Results

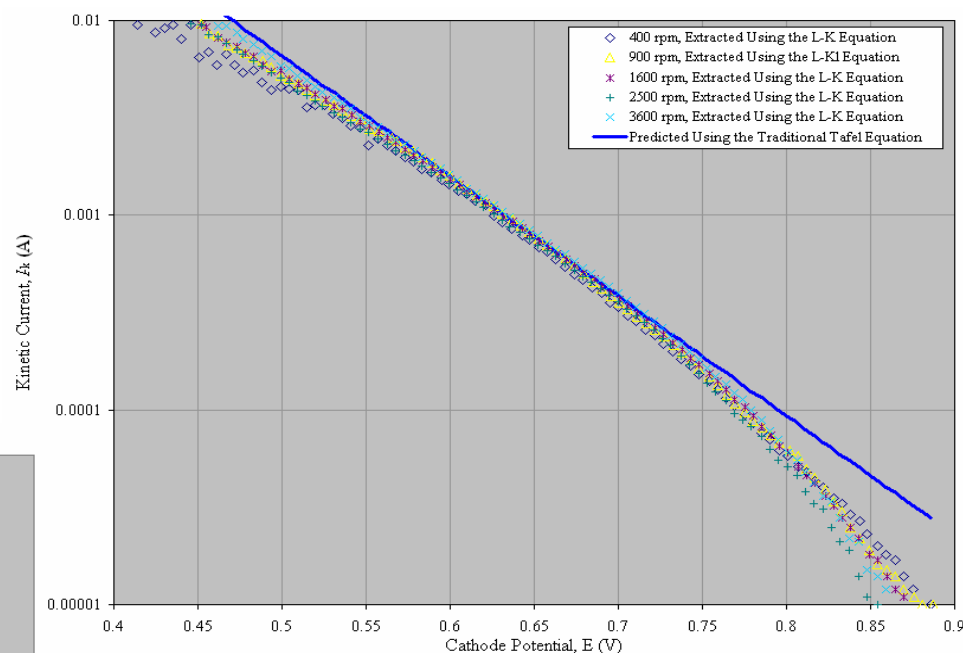
Future Work

- ❖ measure the RDE data over a wide range of temperatures, e.g., 40-80 °C
- ❖ use the semi-empirical kinetic equation to develop an accurate PEM fuel cell model

Goodness of the Semi-Empirical Model in Predicting the ORR Kinetic Current, I_k



Goodness of the Tafel Equation in Predicting the ORR Kinetic Current, I_k



- semi-empirical equation is far superior to the Tafel equation
- using the semi-empirical equation in future PEM fuel cell modeling will improve the accuracy in the evaluation of the relative importance of other transport phenomena



Collaborations

Ritter

Current

- Ragaiy Zidan: SRNL (melt processing and scale-up)
- Chris Williams: USC (Raman spectroscopy studies)
- Vitali Rasolov: USC (*ab initio* studies)
- Alex Angerhofer: UF (EPR studies)

Future

- potential to interact with or become part of the Metal Hydride Center of Excellence at SNL

Weidner

Current

- William Summers: SRNL (Hybrid Sulfur Process)

Future

- Richard Doctor: ANL (Modified Ca-Br Process)
- Michael Simpson: INEEL (Reverse Deacon Process involving HCl)

Matthews

Future

- potential to interact with or become part of the Chemical Hydrogen Center of Excellence



Publications and Presentations

Publications

1. J. Wang, A. D. Ebner and J. A. Ritter, "On the Reversibility of Hydrogen Storage in Novel Complex Hydrides," *Adsorption*, 11, 811-816 (2005).
2. J. Wang, A. D. Ebner, R. Zidan, and J. A. Ritter, "Synergistic Effects of Co-Dopants on the Dehydrogenation Kinetics of Sodium Aluminum Hydride," *J. Alloys and Compounds*, **391**, 245-255 (2005).
3. J. Wang, A. D. Ebner, R. Zidan, and J. A. Ritter, "Effect of Graphite on the Dehydrogenation and Hydrogenation Kinetics of Ti-Doped Sodium Aluminum Hydride," *J. Alloys and Compounds*, in press (2005).
4. T. Prozorov, J. Wang, A. D. Ebner and J. A. Ritter, "Sonochemical Doping of Ti-Catalyzed Sodium Aluminum Hydride," *J. Alloys and Compounds*, submitted (2005).
5. J. Wang, R. C. Petty, A. D. Ebner, T. Prozorov and J. A. Ritter, "Low Temperature Performance of Ti-Doped Sodium Aluminum Hydride with Single Wall Carbon Nanotubes as a Co-Catalyst," *Nanotechnology*, submitted (2005).

Presentations

1. J. Wang, T. Prozorov, A. D. Ebner and J. A. Ritter, "Novel Complex Hydrides for Reversible Hydrogen Storage," AIChE Annual Meeting, Austin, TX, November 2004.
2. Michael A. Matthews, Thomas A. Davis, and Eyma Y. Marrero-Alfonso, "Hydrogen storage in chemical hydrides", ACS National Meeting, Philadelphia, PA, August 2004.
3. Michael A. Matthews, Thomas A. Davis, and Eyma Y. Marrero-Alfonso, "Production of hydrogen from chemical hydrides via hydrolysis with steam", AIChE Annual Meeting, Austin, TX, November 2004.
4. J. W. Weidner, P. Sivasubramanian, R. Ramasamy, C.E. Holland and F. Freire, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," AIChE, Atlanta, GA, April, 2005.
5. J. W. Weidner, P. Sivasubramanian, and F. Freire, "Electrochemical Conversion of Anhydrous HBr to Br₂ for Hydrogen Production," The Electrochemical Society, Honolulu, HI, October, 2004.

Patent Applications

1. R. Zidan, J. A. Ritter, A. D. Ebner, J. Wang and C. E. Holland, "Hydrogen Storage Material and Process Using Graphite Additive With Metal Doped Complex Hydrides, Patent Application, US Patent Application 2005/0032641A1 (2005).
2. J. Ritter, A. D. Ebner, C. H. Holland and T. Prozorov, "Method for Improving the Performance of Metal-Doped Complex Hydrides, Provisional Patent Application, filed February 28 (2005).



Thank You!

**Any
Questions?**